

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE Technical Papers		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER M2C8	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				8. PERFORMING ORGANIZATION REPORT	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS 1121 884					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified		19b. TELEPHONE NUMBER (include area code) (661) 275-5015	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

62

separate items are enclosed

TP-FY99-0112

✓ Spreadsheet
✓ DTS

MEMORANDUM FOR PRR (Contractor/In-House Publication)

27 May 1999

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-0112**
Boatz et al., "Quantum and Classical Monte Carlo and Molecular Dynamics Simulations of the Structures,
Photoionization-induced Fragmentation, and Optical Absorption Spectra of AlAr_N Clusters"
Poster Session HEDM CONFERENCE

(Public Release)

Quantum and Classical Monte Carlo and Molecular Dynamics Simulations of the Structures, Photoionization-induced Fragmentation, and Optical Absorption Spectra of AlAr_N Clusters

Jerry A. Boatz and Jeffrey A. Sheehy

Air Force Research Laboratory

Propulsion Sciences and Advanced Concepts Division

AFRL/PRSP

Edwards AFB, CA 93524

Robert J. Hinde[†]

Department of Chemistry
University of Tennessee
Knoxville, TN 37996

Peter W. Langhoff^{††}

Department of Chemistry
Indiana University
Bloomington, IN 47405

[†] RDL Summer Faculty Research Associate, 1998.

^{††} NRC Senior Research Associate, 1998/1999.

AFOSR High Energy Density Matter Contractors'
Conference, 8-11 June 99

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Jerry A. Boatz and Jeffrey A. Sheehy

Air Force Research Laboratory
Propulsion Sciences and Advanced Concepts Division
AFRL/PRSP
Edwards AFB, CA 93524-7680

Robert J. Hinde[†]
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

Peter W. Langhoff^{††}
Department of Chemistry
Indiana University
Bloomington, IN 47405-4001

ABSTRACT

The theory group at AFRL/PRSP is engaged in an ongoing effort to develop, implement, and test the spectral theory of Schrödinger eigenstates for efficient construction of accurate many-body potential energy surfaces for HEDM systems such as atoms embedded in solid hydrogen. Because good experimental data is available for AlAr_N clusters, they make an excellent test bed for the spectral theory and its computational implementation. We have used the spectral theory method to calculate the ground and low-lying excited states of AlAr_N clusters, subsequently employing these in a sequence of quantum and classical Monte Carlo and classical molecular dynamics simulations to predict their structures, photoionization-induced fragmentation pathways, and optical absorption spectra. These simulations address the key issue of the degree of cluster fragmentation encountered following photoionization of the neutral clusters. The measured data refer to ion mass spectrometric signals of $[\text{AlAr}_{N-M}]^+$ fragments detected subsequent to one-photon uv excitation followed by visible one-photon ionization of a distribution of non size-selected parent AlAr_N clusters. Thus, the observed spectrum attributed to AlAr_{N-M} is actually a superposition of spectra of all parent neutral clusters AlAr_N which produce $[\text{AlAr}_{N-M}]^+$ as one of the ionic fragments following the photoionization step. The simulations involve three steps: (1) generation of the ground state wavefunction ψ of the parent neutral AlAr_N cluster using diffusion quantum Monte Carlo methods, (2) vertical excitation of an ensemble of configurations drawn from the ground state probability density $|\psi|^2$ to the $[\text{AlAr}_N]^+$ ionic surface, followed by classical molecular dynamics simulations of the relaxation and fragmentation processes leading to formation of a distribution of fragment ions $[\text{AlAr}_{N-M}]^+ + M \text{ Ar}$; $M=1,2,3,\dots$, and (3) classical Monte Carlo simulations of a "hybrid" absorption spectrum as a weighted average of the predicted spectra of the neutral clusters AlAr_N contributing to the formation of the ionic $[\text{AlAr}_{N-M}]^+$ fragment.

[†] RDL Summer Faculty Research Associate, 1998.

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GOAL


Stabilize up to 5% atoms in solid hydrogen.

OBJECTIVES

Develop, implement, and apply efficient computational methods for reliable prediction of properties (e.g., structures, stabilities, electronic and vibrational spectra) of doped cryogenic solids.

APPROACH

Develop efficient computational methods for reliable modelling and simulation of advanced cryogenic propellants such as boron atoms in solid hydrogen, including (a) construction of accurate potential energy surfaces using the spectral theory of Schrödinger eigenstates, (b) reliable methods for proper treatment of quantum effects such as tunnelling and zero-point energies (e.g., diffusion quantum Monte Carlo, path integral Monte Carlo, Centroid Molecular Dynamics), and (c) development of models for reliable prediction of laboratory observables (electronic absorption and emission, vibrational spectra))



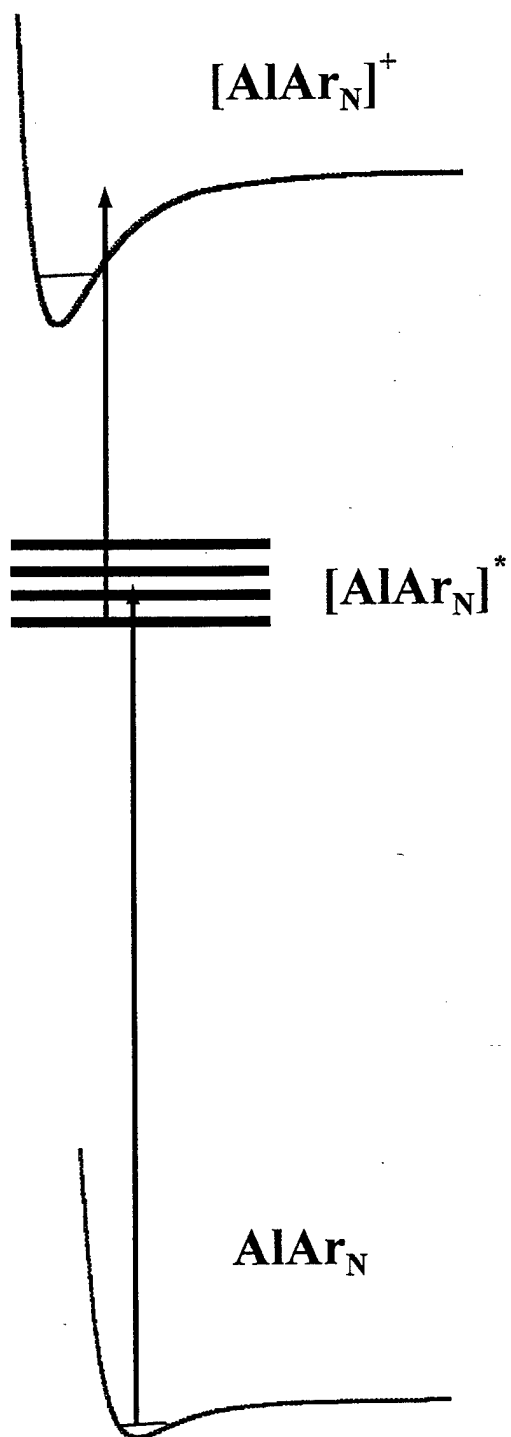
OVERVIEW

Although AlAr_N clusters are not HEDM, they are nonetheless useful prototypes for actual HEDM systems such as $\text{B}(\text{H}_2)_N$ clusters and solids. Because good experimental data is available for AlAr_N clusters (including information on ground and excited state potential energy surfaces), they make an excellent test bed for our new spectral theory of Schrödinger eigenstates and its computational implementation.

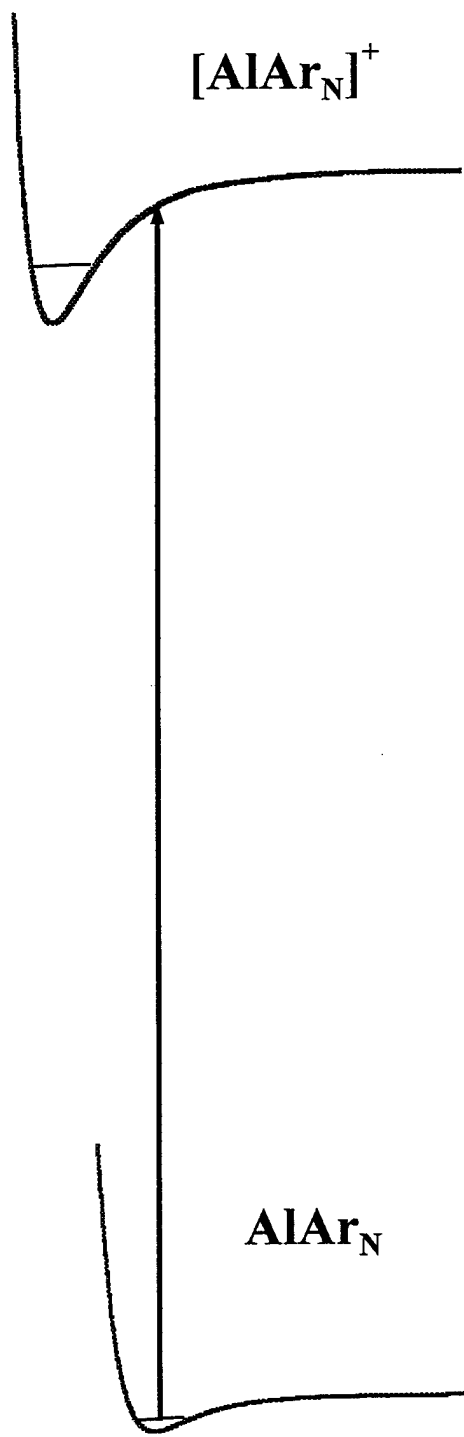
EXPERIMENTS

AlAr_N clusters are generated by laser vaporization of aluminum metal and supersonic expansion of an Ar carrier gas. The clusters are then ionized by 1+1' two-color multiphoton ionization, first exciting the Al atom $3p \rightarrow 3d$ transition with the doubled UV photon and subsequently ionizing with the visible fundamental photon. Following ionization, the clusters are detected using TOF mass spectrometry.

Experiment



Simulation



SIMULATION PROTOCOL

1. DQMC: Ground state wavefunction of neutral AlAr_N parent cluster is represented by collection of 500 "walkers", which are equilibrated for 10-20 ps.
2. Each "walker" provides an initial configuration for an MD trajectory on the ionic potential energy surface. Vertical excitation from ground state surface to ionic surface is followed by 250 ps trajectory.
3. The size of the cluster at the end of each MD trajectory in step 2 is weighted by the proper descendant weight of the originating walker. Results are averaged over all walkers to obtain predicted fragmentation pattern.
4. Absorption spectra of each neutral cluster AlAr_N which produces a fragment of size AlAr_{N-M} is simulated using AlAr_N ground and excited state potentials constructed by spectral theory method, used in conjunction with classical Monte Carlo simulations for ensemble averages of AlAr_N cluster geometries.
5. A "hybrid" spectrum is constructed as a weighted average of the spectra of the parent clusters, using the distribution of fragment sizes obtained in step 3. Uniform distribution of parent neutral clusters is assumed!

SPECTRAL THEORY OUTLINE

Diatomic wavefunctions written as superposition of atomic product states (direct product of Al and Ar atomic states):

$$\begin{array}{cc} \text{Al} & \text{Ar} \\ \{3P, 4S, 3D, 4P\} \otimes \{^1S_0\} \end{array}$$

$$\begin{aligned} \Phi &= \{ 3P_{+1} \bullet ^1S_0, 3P_0 \bullet ^1S_0, 3P_{-1} \bullet ^1S_0, 4S \bullet ^1S_0, 3D_{+2} \bullet ^1S_0, \dots, 4P_{-1} \bullet ^1S_0 \} \\ &= \{ 3P_{+1}, 3P_0, 3P_{-1}, 4S, 3D_{+2}, \dots, 4P_{-1} \} \end{aligned}$$

$$\Psi = \{ X \ ^2\Pi, A \ ^2\Sigma, B \ ^2\Sigma, \dots, (3) \ ^2\Pi \}$$

$$\Phi = U^t \Psi$$

Hamiltonian for atomic cluster given by:

$$H = \sum H^{(k)} + H^{(SO)}$$

$$H^{(k)} = D^t(\theta_k, \phi_k) U^t(R_k) E(R_k) U(R_k) D(\theta_k, \phi_k) - E^{(0)}$$

$$H^{(so)} = \text{spin-orbit coupling operator for Al atom.}$$

$$E = \text{diagonal matrix of diatomic interaction energies (X,A,B,C,... state energies)}$$

U = unitary matrix which transforms from the diatomic basis to the atomic-product basis.

D = transformation matrix connecting the "rotated" and laboratory coordinate systems.

Atomic state mixing parameters U_{ij} obtained from eigenvectors of the diatomic and "spectral-product" transition moment matrices: $U = U_d (U_{sp})^t$, where U_d and U_{sp} obey the following:

$$\lambda_d = (U_d)^t \mu(R) U_d$$

and

$$\lambda_{sp} = (U_{sp})^t \mu_0(R \rightarrow \infty) U_{sp}$$

If $\lambda_{sp} = \lambda_d$, then

$$(U_d)^t \mu(R) U_d = (U_{sp})^t \mu_0 U_{sp}$$

$$(U_{sp}) (U_d)^t \mu(R) U_d (U_{sp})^t = \mu_0$$

$$U^t \mu(R) U = \mu_0$$

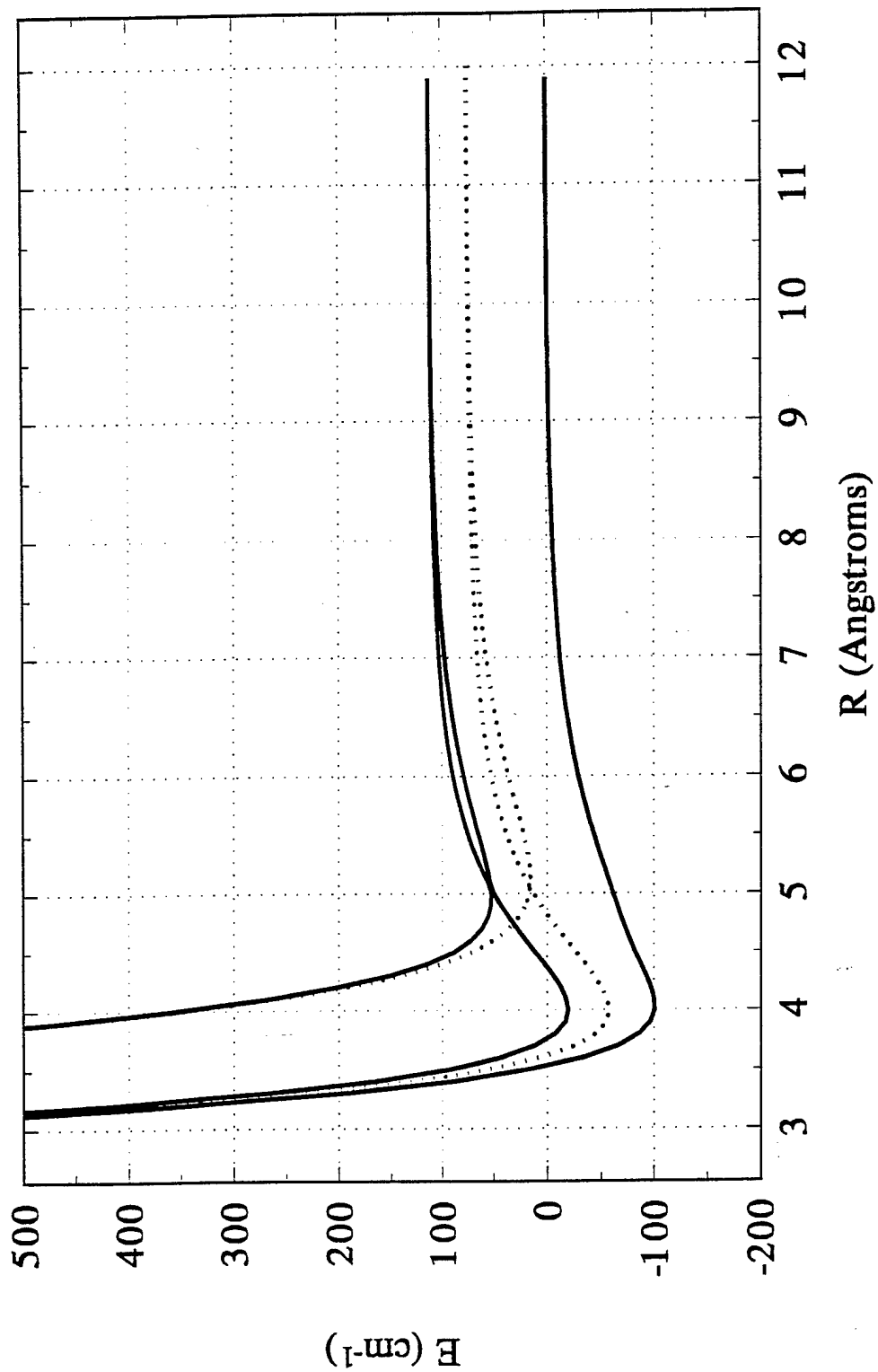
This is "exact" only in the case where $\lambda_{sp} = \lambda_d$.

U is related to diatomic nonadiabatic coupling matrix elements. If $P_{ij}(R) = \langle \Psi_i | d/dR | \Psi_j \rangle$, then

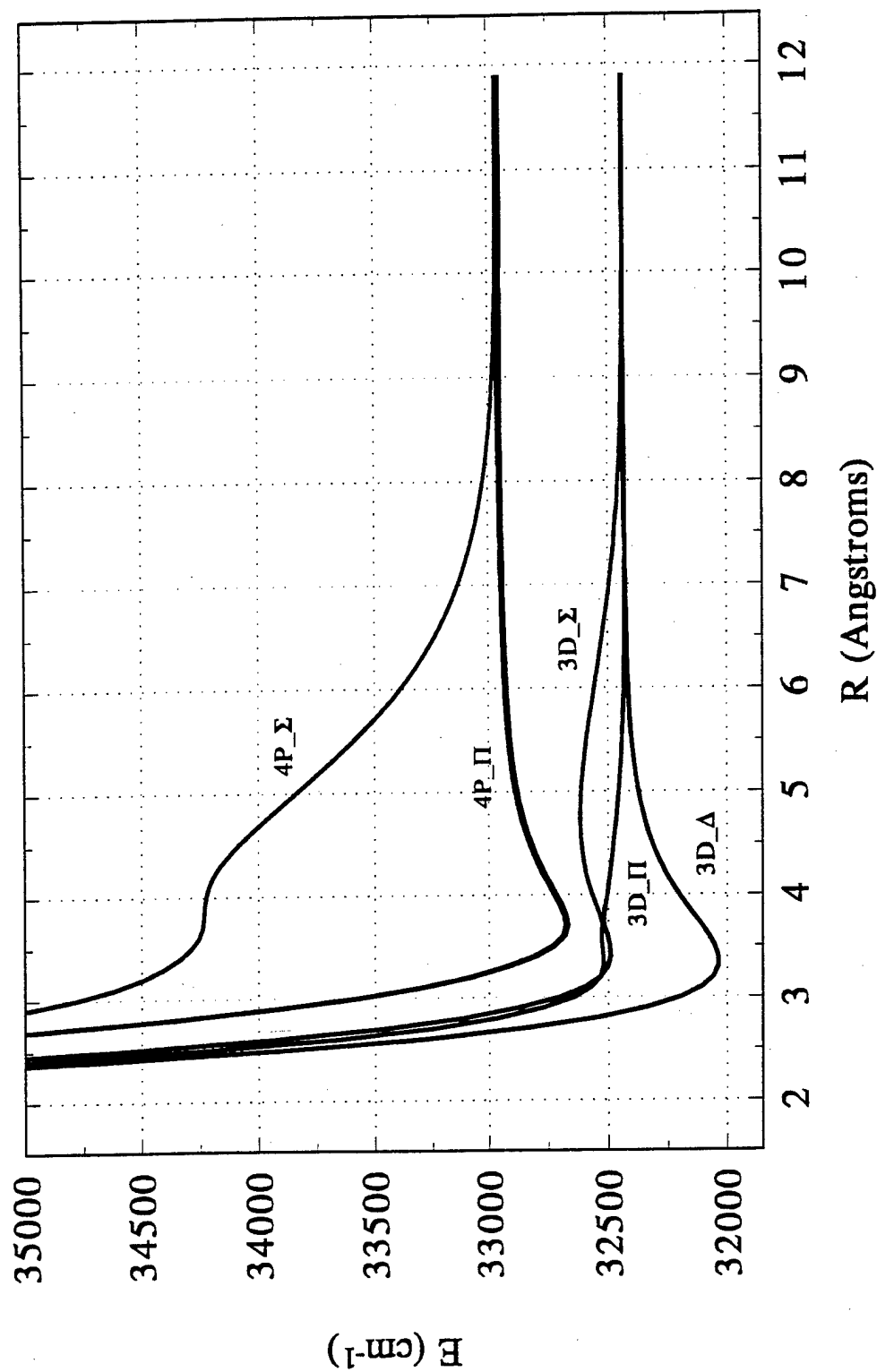
$$dU/dR + PU = 0 \implies P = - (dU/dR) U^t$$

(Werner and Meyer, JCP 74, 5802 (1981))

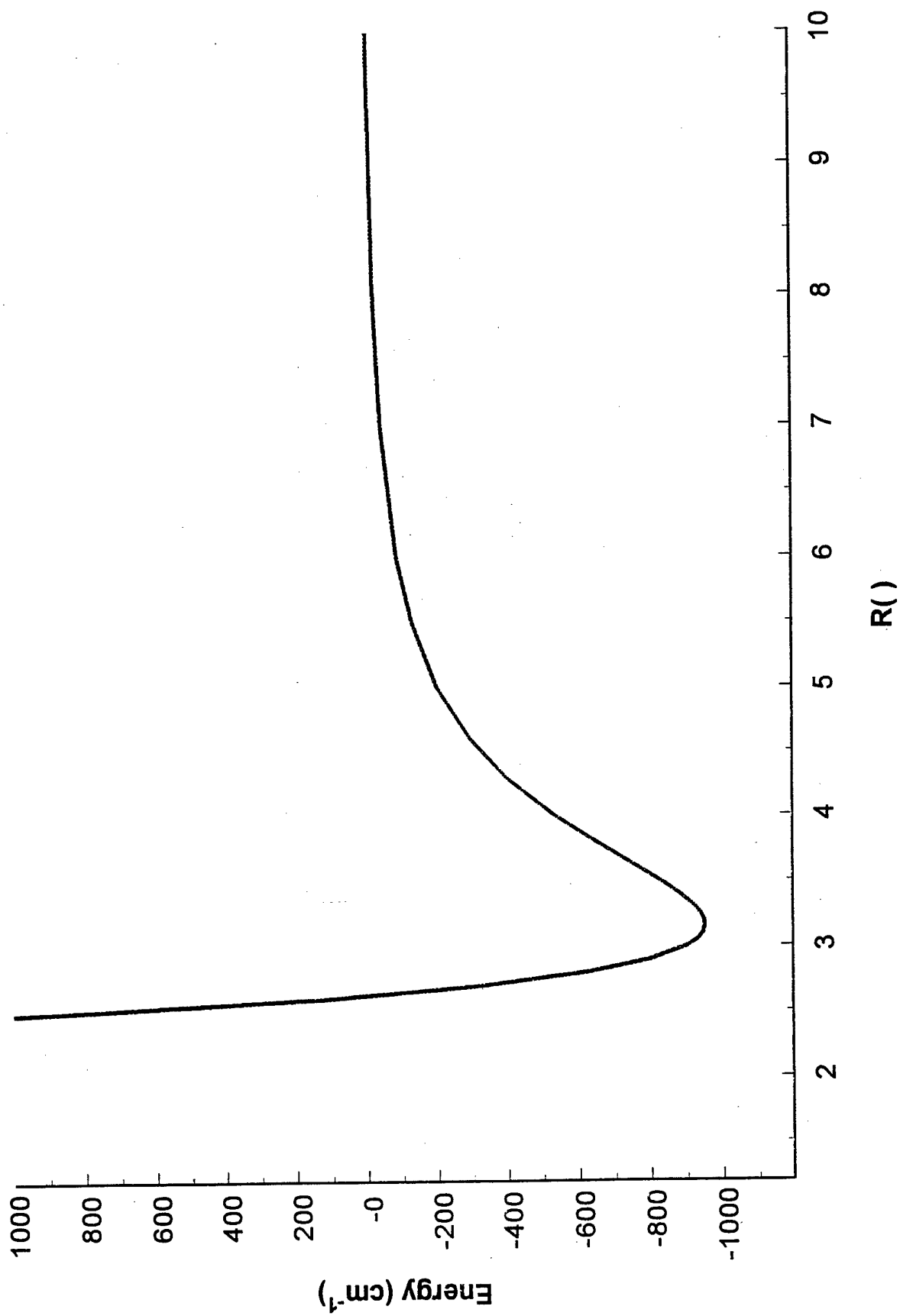
AlAr MRCI Potentials "3P" curves



AlAr MRCI Potentials "3D,4P" curves



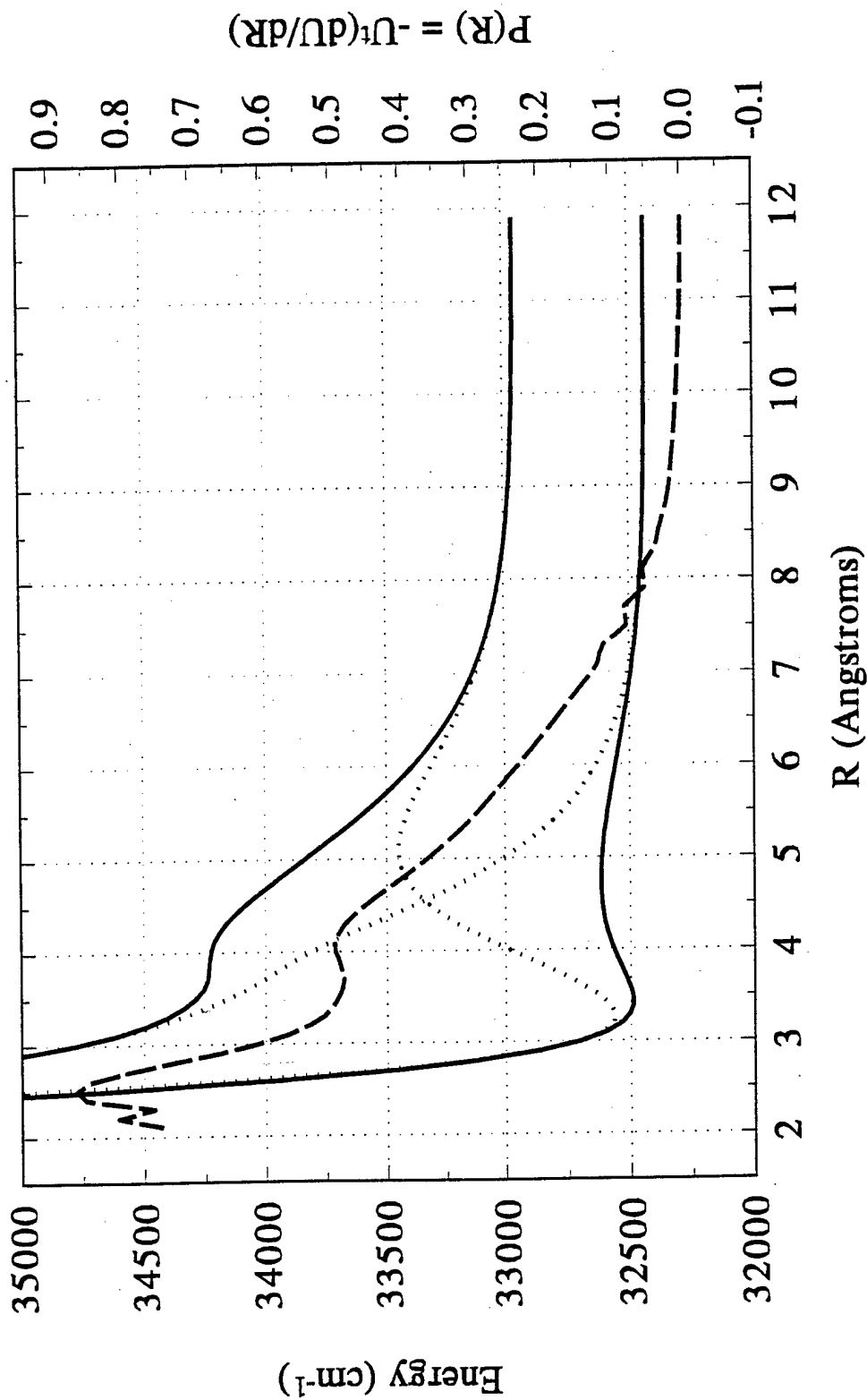
[Al-Ar]⁺ Ground State Potential
CCSD(T)/cc-aug-v5z(-h), corrected for BSSE



Al-Ar MRCI Potentials

Adiabatic (solid) and Diabatic (dots) 3D,4P Σ Potentials

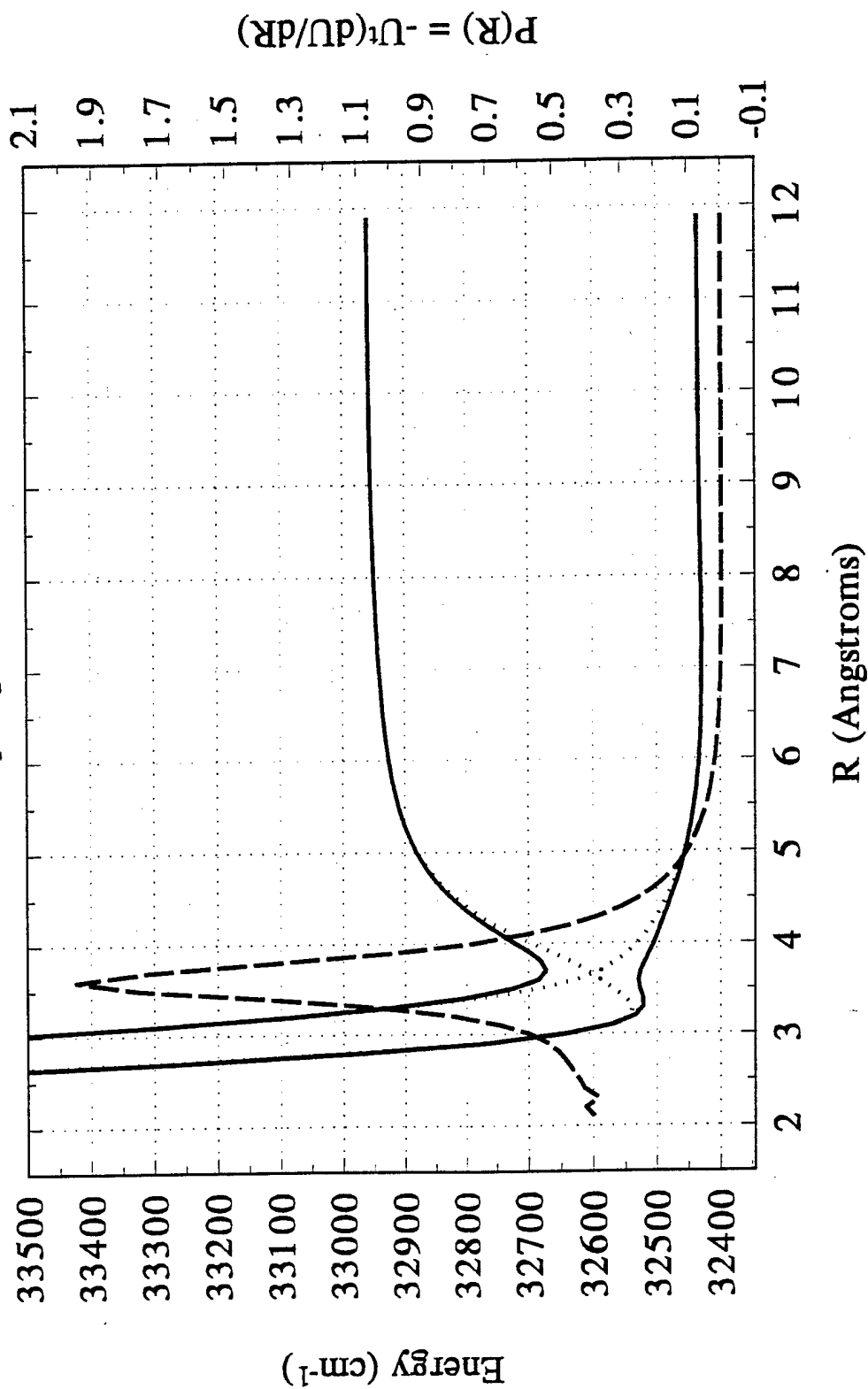
Non-adiabatic coupling element (dashed curve)



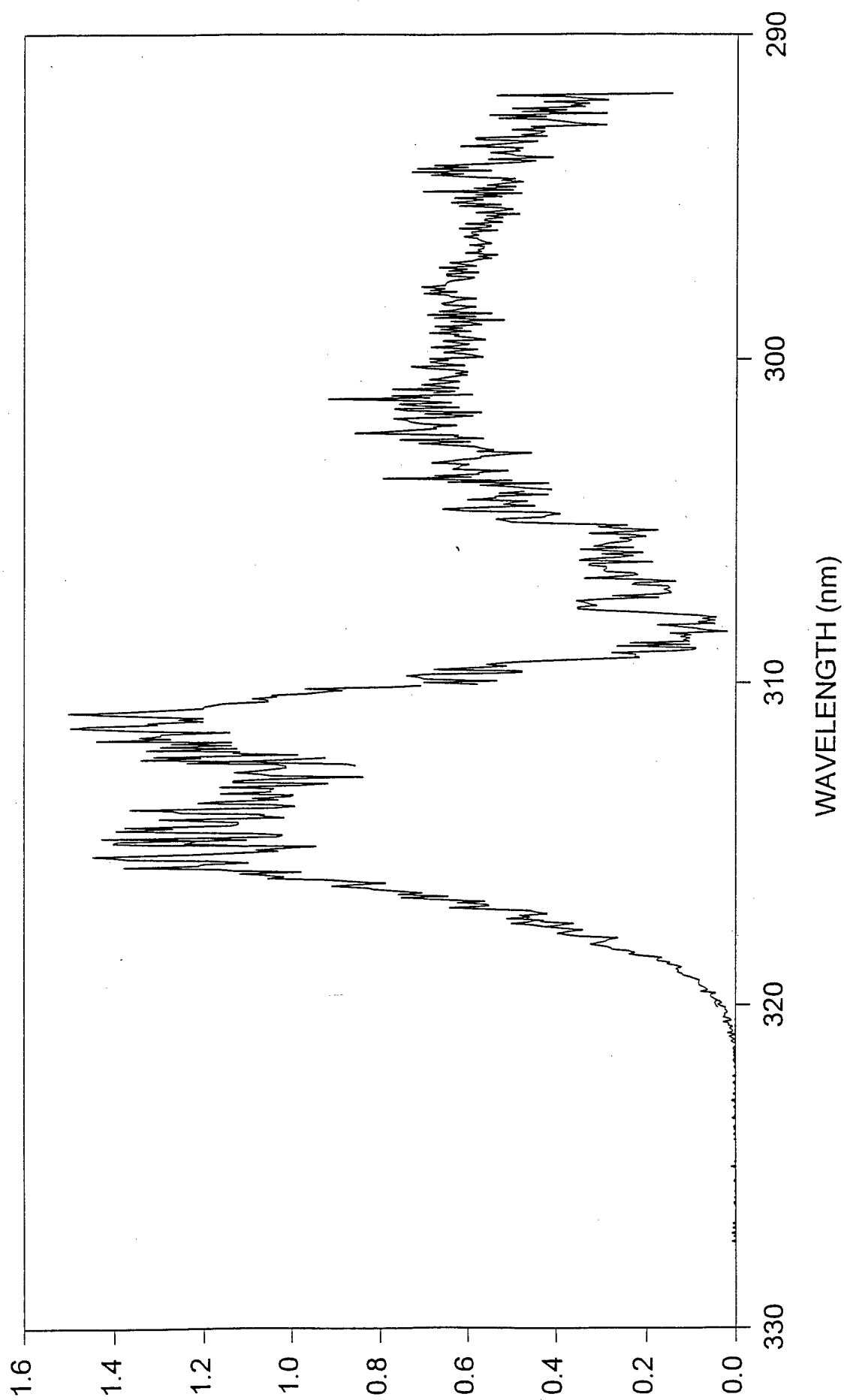
Al-Ar MRCI Potentials

Adiabatic (solid) and Diabatic (dots) 3D,4P Π Potentials

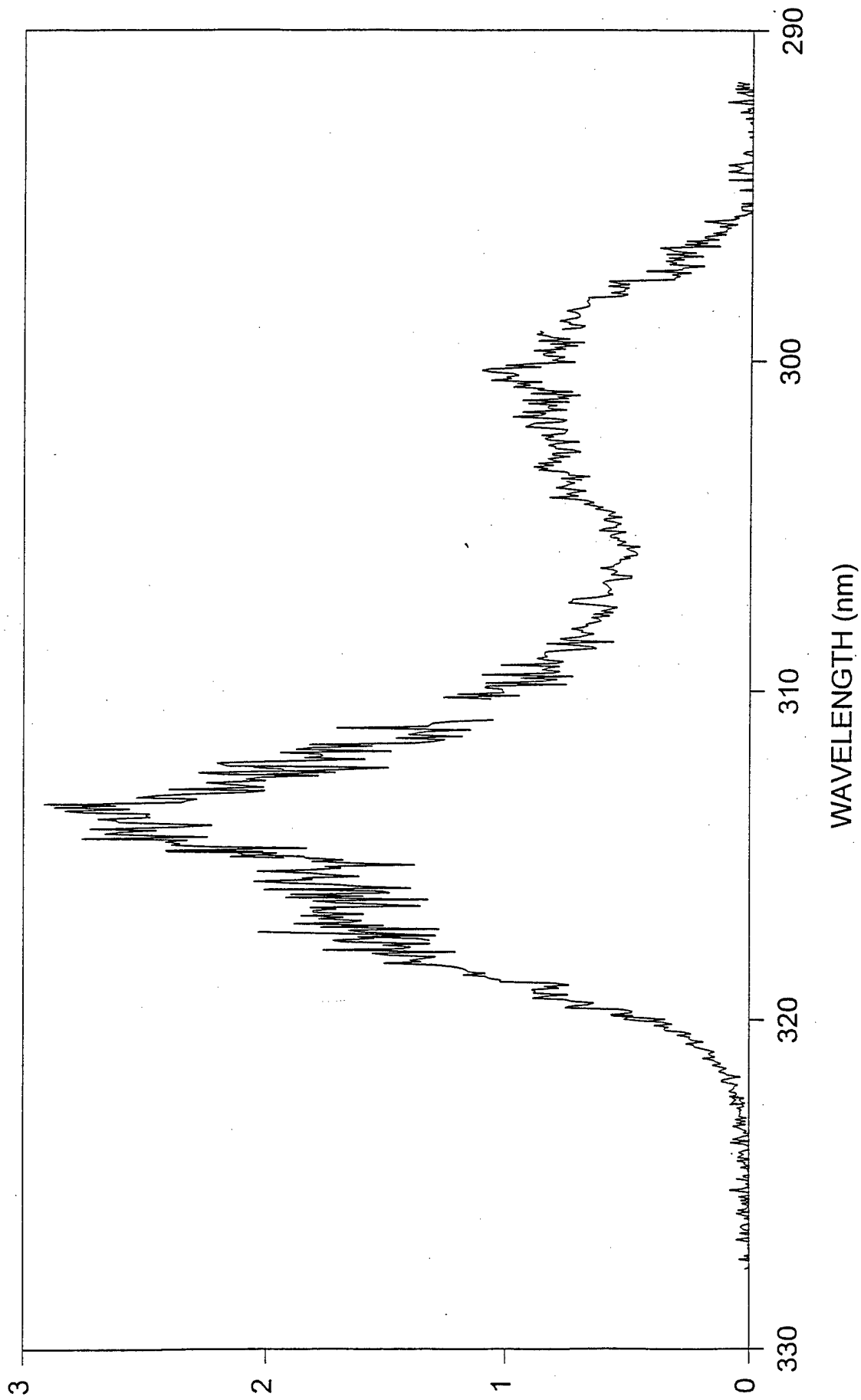
Non-adiabatic coupling element (dashed curve)



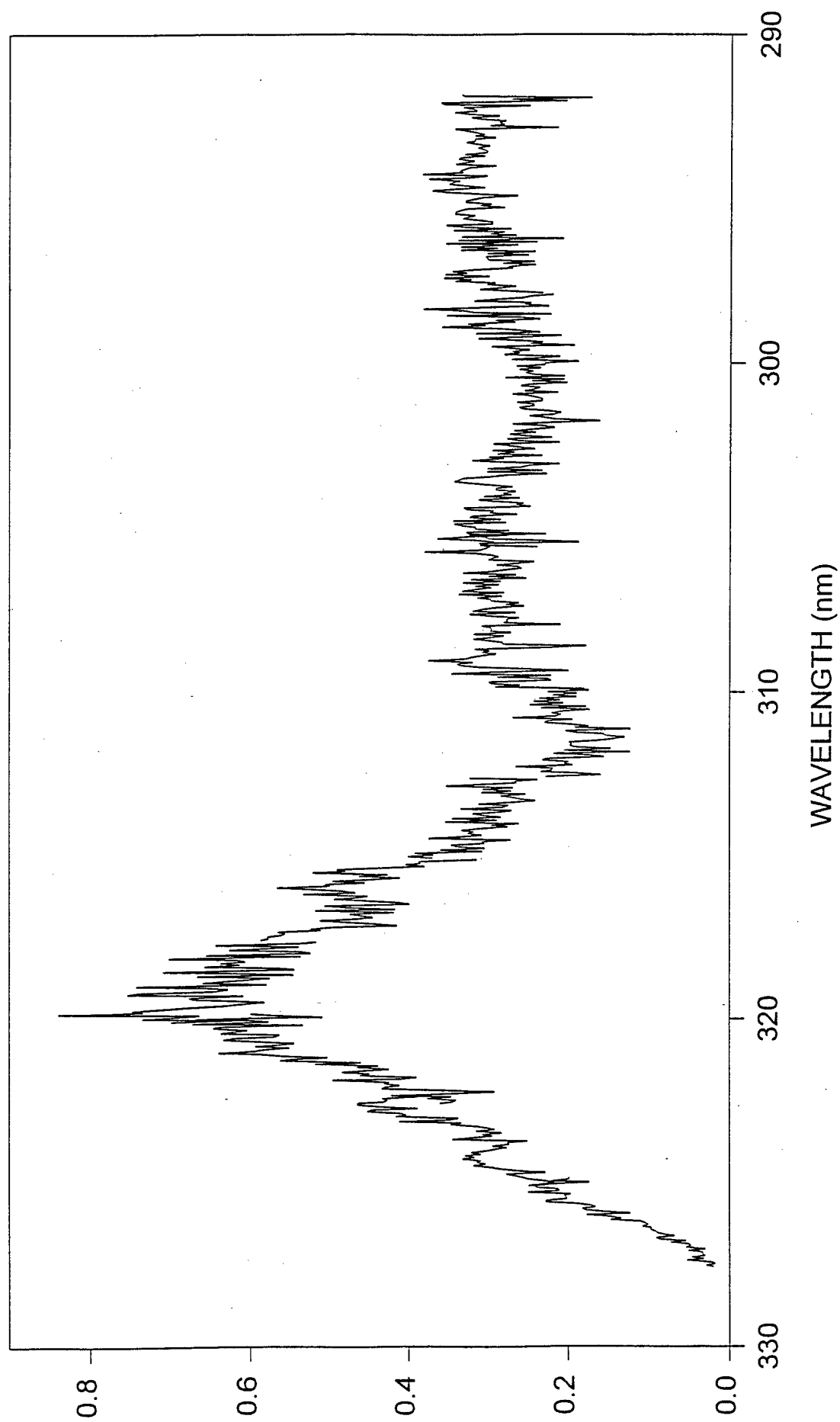
AlAr₆



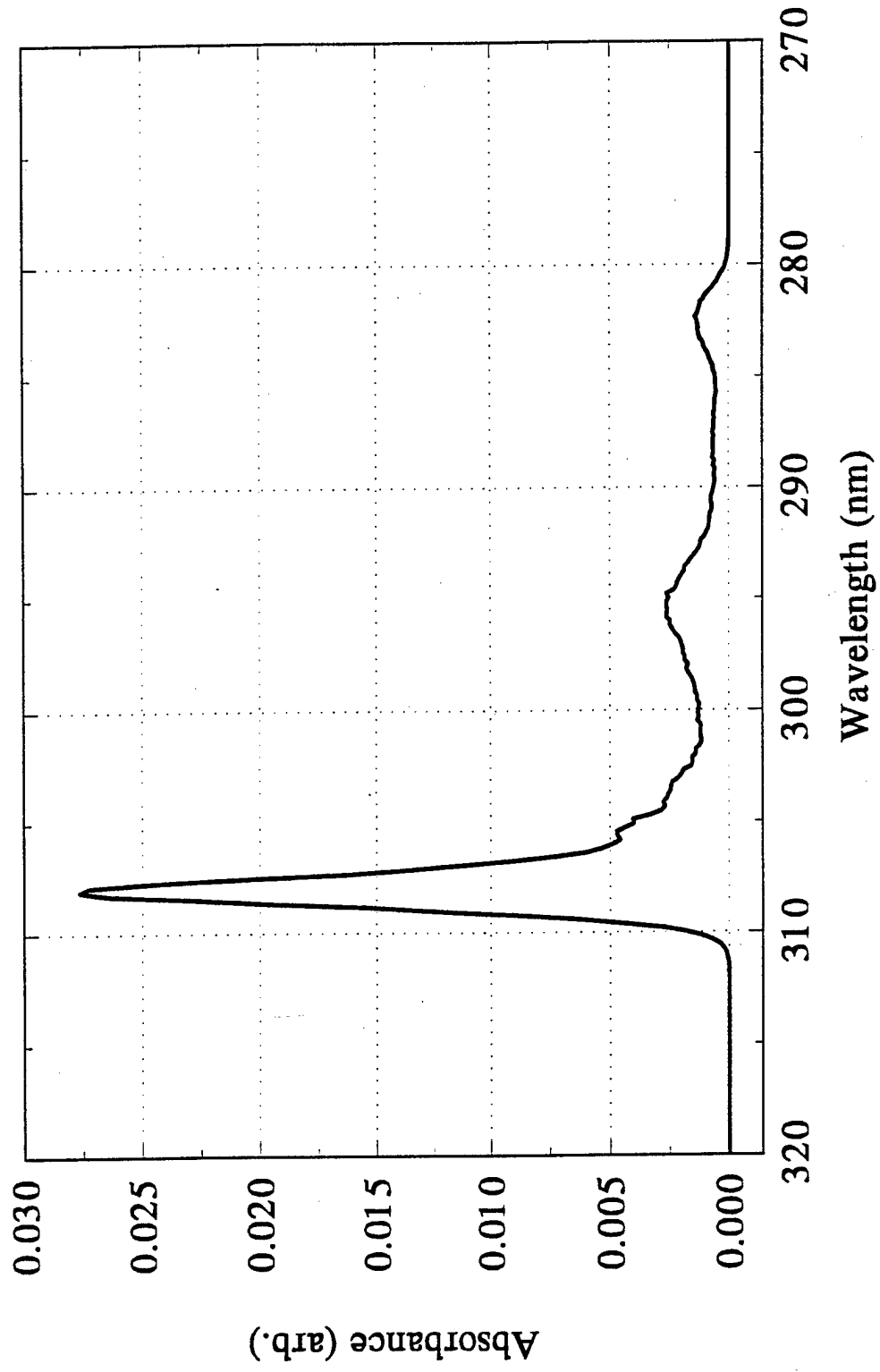
AlAr₁₂



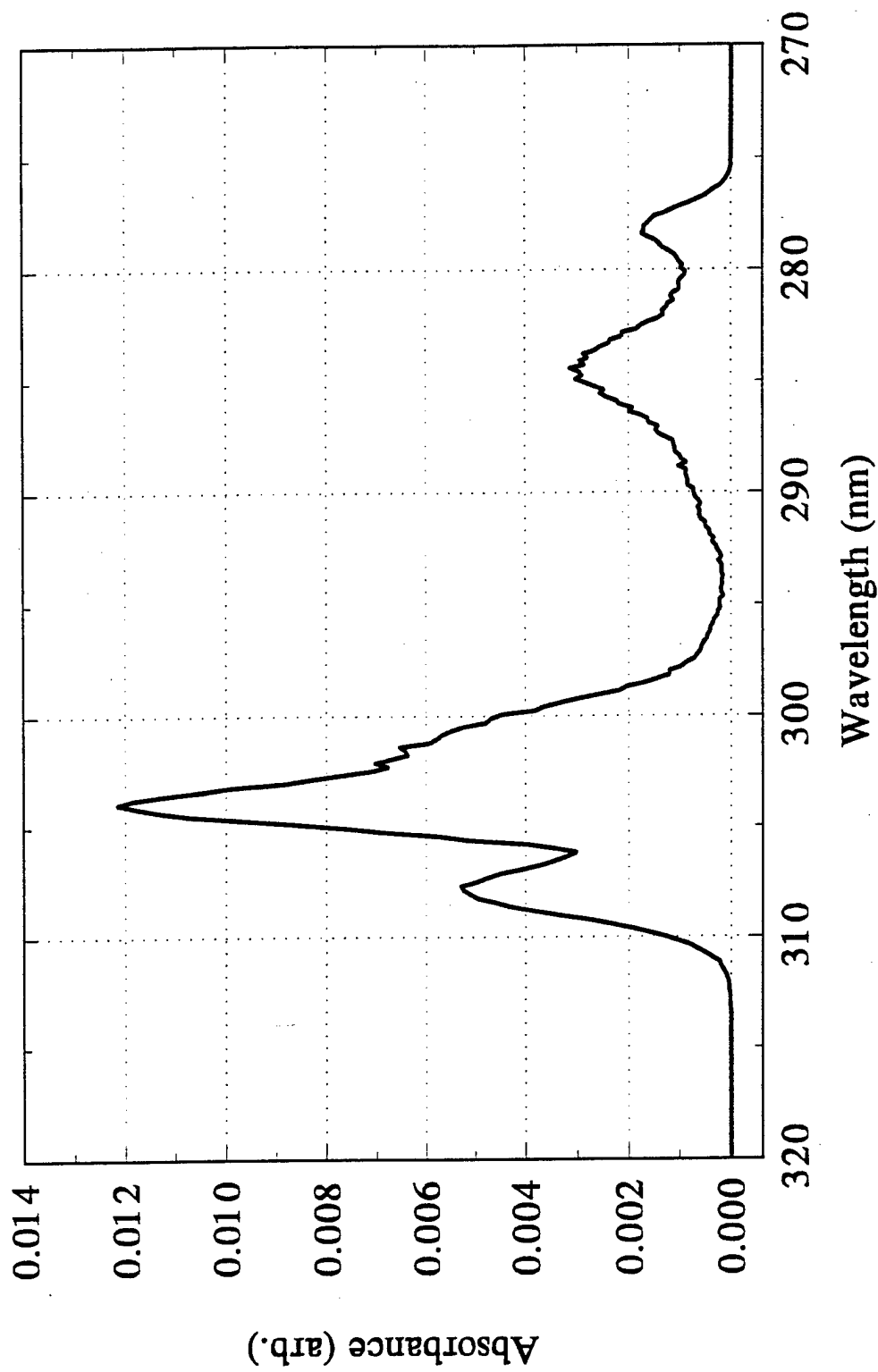
AlAr₅₄



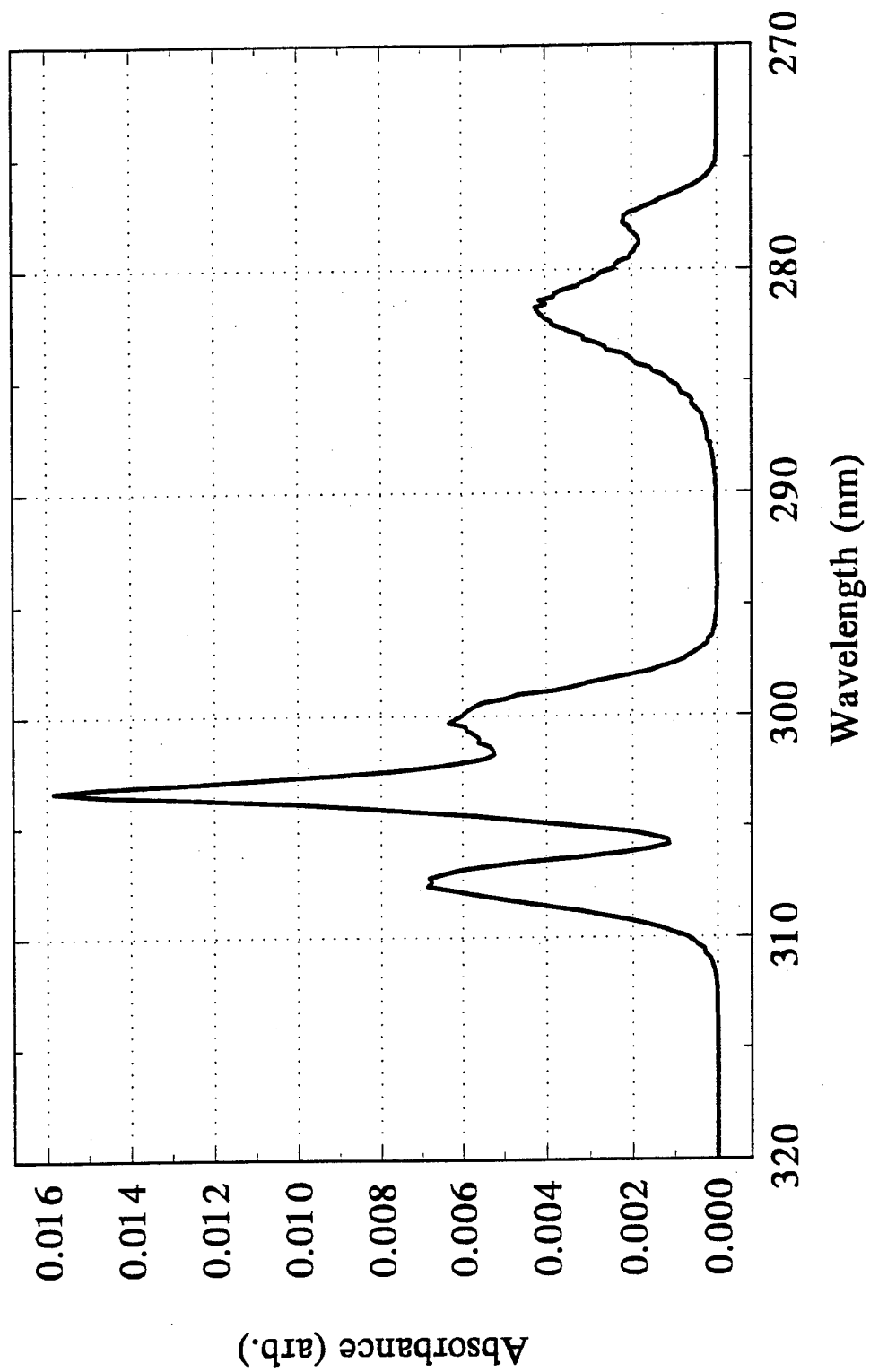
Al-Ar6 Absorption Spectrum
T = 30K, ST



Al-Ar12 Absorption Spectrum
T = 30K, ST



Al-Ar54 Absorption Spectrum
T = 30K, ST

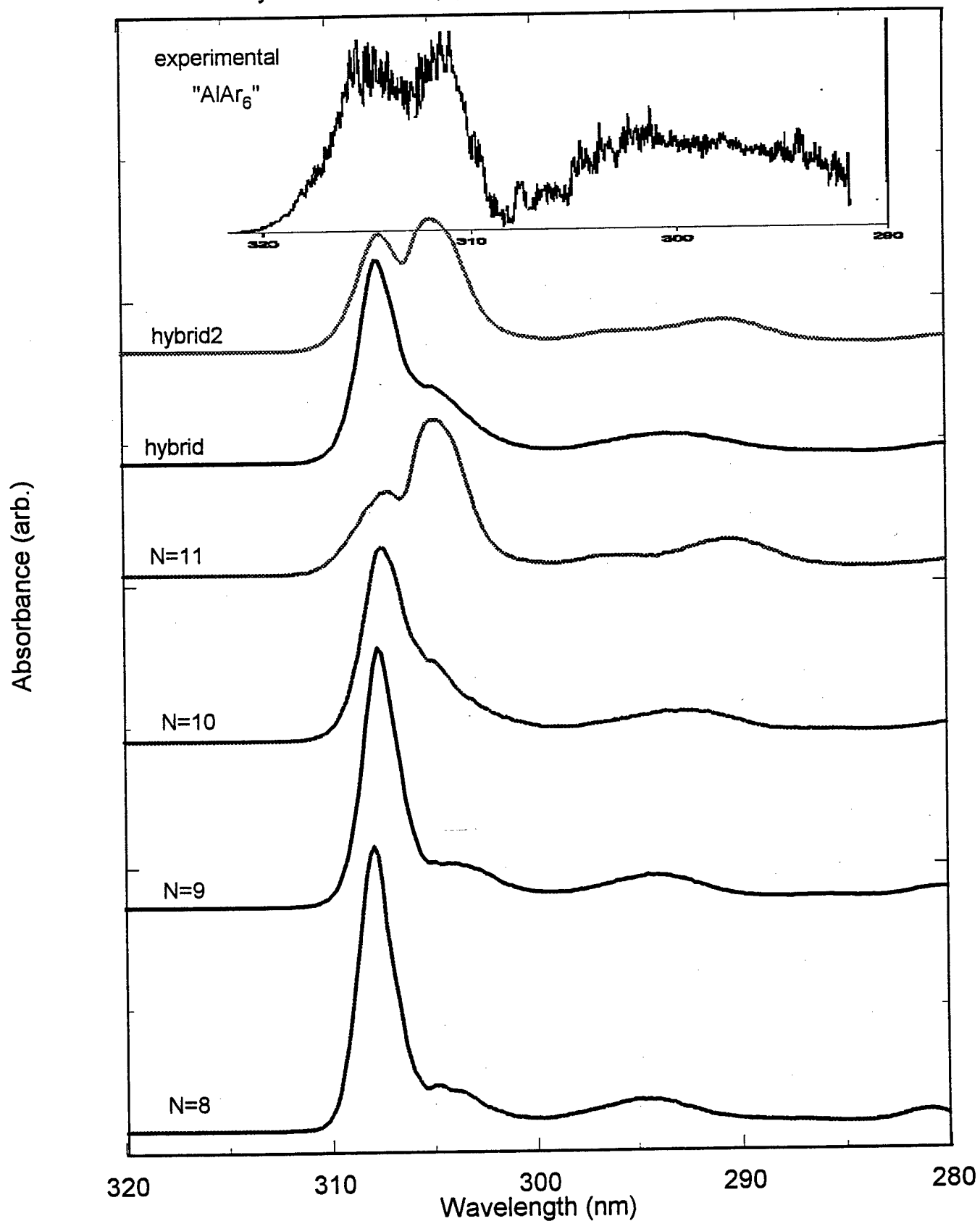


AlAr_N Absorption Spectra

N=8-11; T = 30K

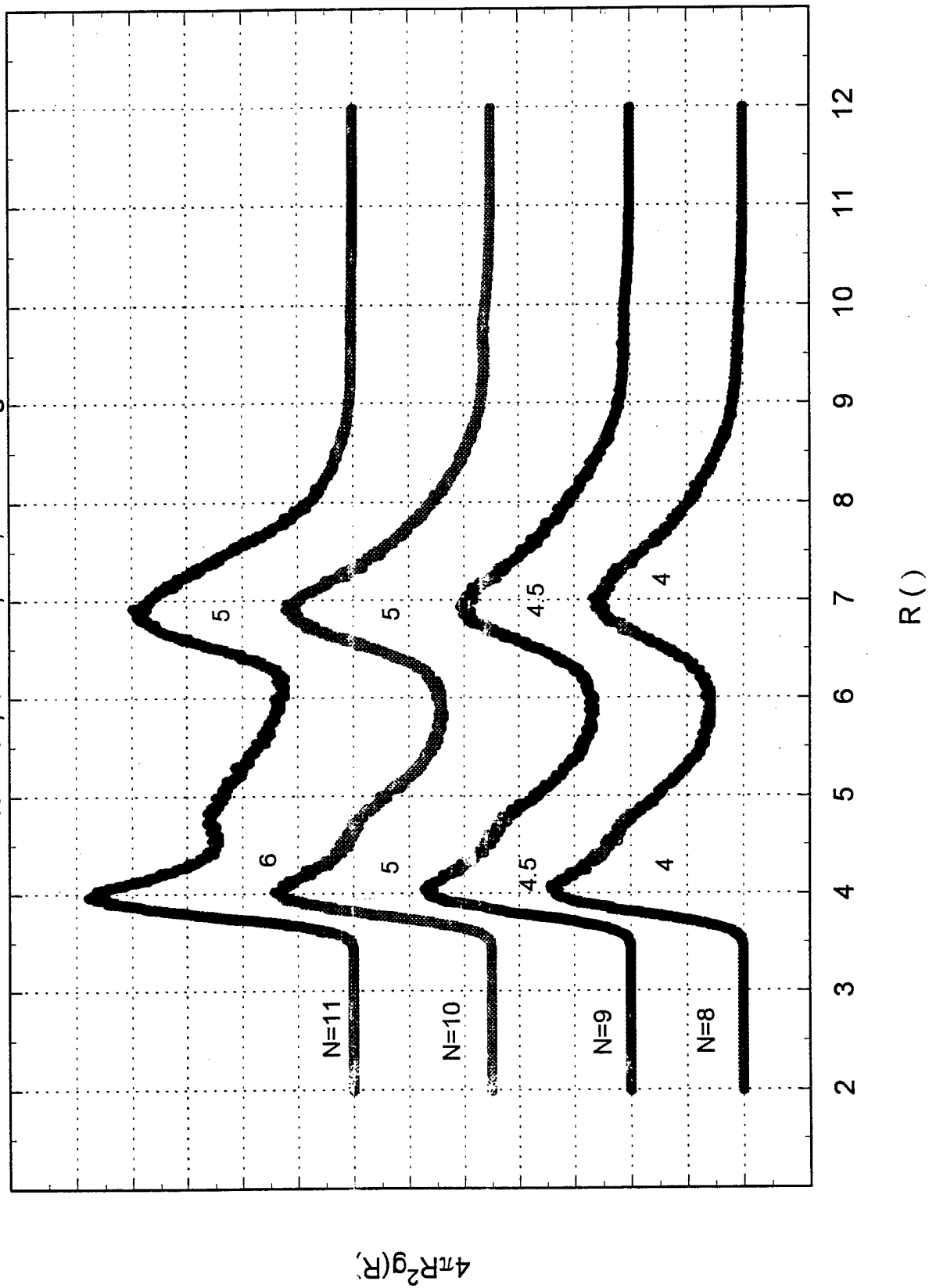
$$\text{"hybrid"} = 0.057(8) + 0.345(9) + 0.460(10) + 0.138(11)$$

$$\text{"hybrid2"} = 0.125(9) + 0.125(10) + 0.75(11)$$



AlAr_N Radial Probability Distribution Functions

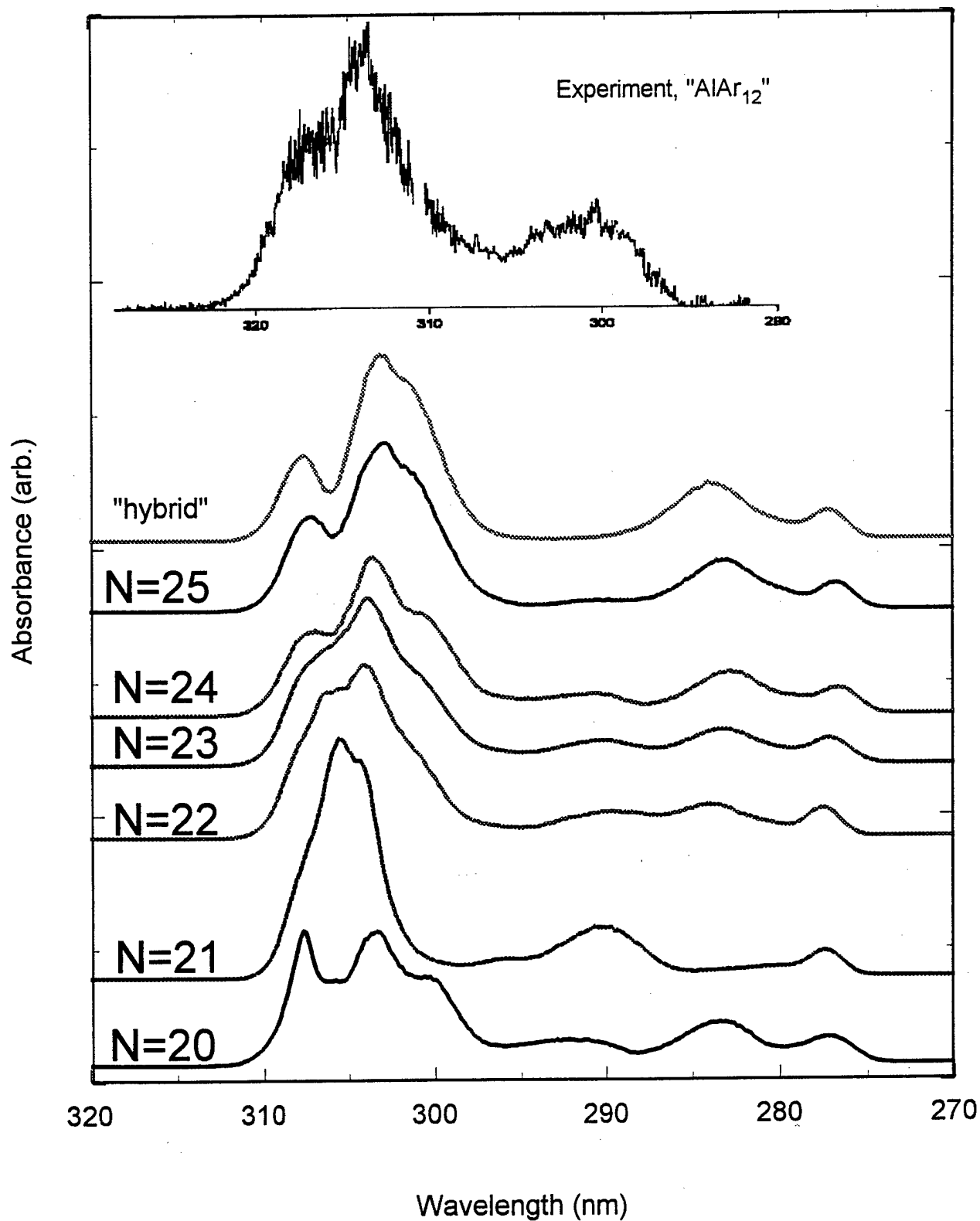
N=8-11; T = 30K, 130,000 configs



AlAr_N Absorption Spectra

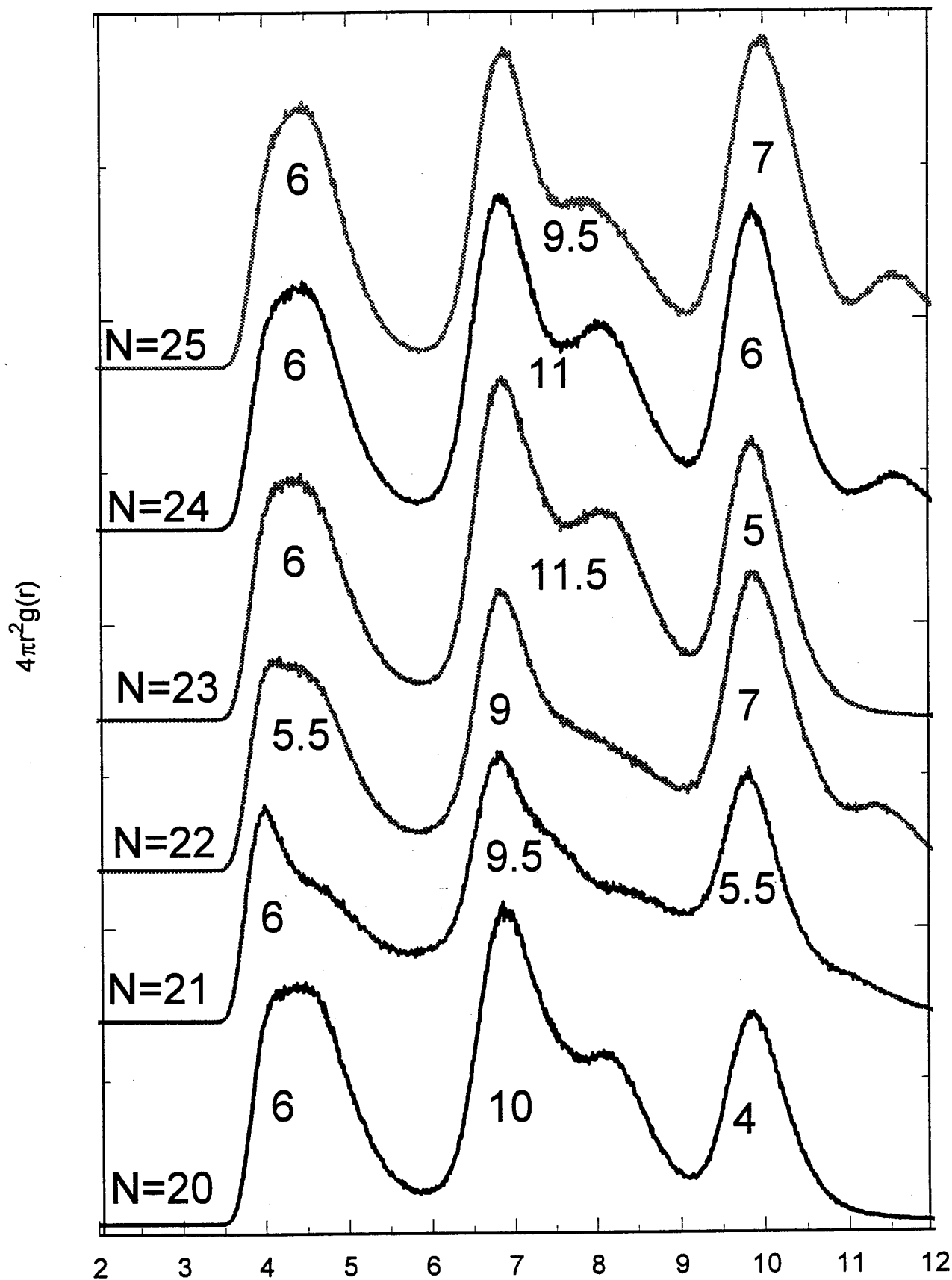
N=20-25; T = 30K

$$\text{"hybrid"} = 0.021(20) + 0.19(21) + 0.24(22) + 0.30(23) + 0.18(24) + 0.077(25)$$



AlAr_N Radial Probability Distribution Functions

N=20-25; T= 30K



CONCLUSIONS

1. Al is located on surface of clusters. Anisotropy of Al-Ar ground state potential energy surface favors surface site for Al atom.
2. Several Ar atoms (2-13) evaporate from the neutral parent AlAr_N clusters following photoionization.
3. The observed and simulated spectra assigned to the AlAr_{12} cluster are in reasonably good agreement. Less satisfactory agreement between theory and experiment is obtained for AlAr_6 . This discrepancy may be due to the assumption of equal populations of the parent neutral clusters AlAr_N .
4. Spectral theory method is a computationally efficient method for calculation of reliable ground and excited state condensed phase potential energy surfaces. Spectral theory properly accounts for avoided crossings of adiabatic potentials.
5. Our model for predicting electronic absorption spectra of atom-doped rare gas solids and clusters shows overall satisfactory agreement with experiment.

FUTURE DIRECTIONS

1. Simulate relaxation on the $[\text{AlAr}_N]^*$ intermediate excited state surface(s) prior to excitation to the ionic state.
2. Incorporate non-additivity into ground state potential energy surfaces (both Al-Ar and Ar-Ar non-additive contributions)
3. More accurate treatment of spin-orbit effects (recalculate diatomic potential curves, including SO)
4. Combine spectral theory potential energy surfaces with quantum simulation method (diffusion MC, CMD)

ACKNOWLEDGEMENTS

Dr. Mario Fajardo

Professor Mitchio Okumura and James M.
Spotts, CalTech

Maui High Performance Computing Center